

AMENDED SPECIFICATION

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PATENT SPECIFICATION

558,881



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Complete Specification Accepted: Jan. 26, 1944.

COMPLETE SPECIFICATION

Improvements in or relating to Methods of Isomerizing

Polyunsaturated Fatty Acids and to Drying Oils

Prepared therefrom

(Communication from AMERICAN CYANAMID COMPANY, a corporation organised under the laws of the State of Maine, United States of America, of 30, 5 Rockefeller Plaza, City and State of New York, United States of America).

I, ARTHUR HAROLD STEVENS, B.Sc. (Lond.), F.C.S., Fellow of the Chartered Institute of Patent Agents, a Subject of the King of Great Britain, of the Firm of Stevens, Langner, Parry & Rollinson, of 5/9, Quality Court, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what 10 manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements 15 in drying oils and the higher fatty acids which they contain. The invention includes the preparation of such oils by isomerizing polyunsaturated higher fatty acids to bring about a relatively high content of conjugated double bonds 20 therein followed by esterification of the isomerized acids with a polyhydric alcohol. The invention also includes a new and improved method of isomerizing polyunsaturated fatty acids as well as 25 certain new drying oils prepared therefrom.

It is known that the drying properties 30 of polyunsaturated higher fatty acids, when employed in the form of triglycerides, oil-modified alkyd resins and the like, are influenced by the positions of their double bonds with respect to each other. If these double bonds are in conjugation (i.e. separated by only one single 35 bond) the oil has better drying properties than a similar oil having an equal number of non-conjugated double bonds. Thus, for example, tung oil dries faster 40 than linseed oil because the three double bonds of the eleostearic acid found in tung oil are in conjugation whereas the double bonds of the linoleic and linolenic acids of linseed oil are not. It is a principal object of the present invention to provide a relatively quick and inexpensive method of isomerizing polyunsaturated higher fatty acids to bring 45 the double bonds thereof into conjugation so that the polyhydric alcohol esters thereof will have improved drying properties.

The present invention provides in a method of isomerizing higher aliphatic polyolefinic monocarboxylic acids to increase the degree of conjugated 50 unsaturation thereof, the step of heating an aqueous solution of soaps thereof and an excess of alkali in a closed chamber at temperatures of 200—250° C. and under the corresponding autogenic pressure for 55 a period of time sufficient to effect substantial conjugation in the polyunsaturated higher aliphatic monocarboxylic acids and discontinuing the heating before excessive polymerization of the 60 unsaturated acids has taken place.

It has been found that the double bonds of polyunsaturated higher fatty acids are brought into conjugation within a few hours by heating an aqueous solution of the soaps thereof with excess alkali in a pressure vessel at temperatures above 200° C. and under the corresponding autogenic pressures. It has also been 65 found that by heating the acids at these 70 temperatures in the form of a solution of their soaps in water the isomerization or rearrangement of the double bonds proceeds much faster than would otherwise 75 be the case, and an equilibrium favouring a relatively high content of conjugated double bonds is reached in from 80 one to three hours. The most favourable 85

temperature range appears to be from 200° to 250° C., for above this range excessive losses of the acids by polymerization may occur.

5 Insofar as it has been possible to determine, the invention is perfectly general in character and may be used for the isomerization of any unsaturated fatty acid or acids the molecules of which contain at least two non-conjugated double bonds. In most cases the isomerization treatment will be applied to mixed fatty acids only some of which are poly-unsaturated as this is the form in which 10 these acids are found in vegetable and fish oils of relatively high iodine values. It is an important advantage of the invention, however, that it can be applied with success to fatty acid mixtures containing relatively low percentages of non-conjugated, polyunsaturated fatty acids, as is the case in soya bean fatty acids, as well as to the more highly polyunsaturated fatty acid 15 mixtures such as those of linseed oil.

The isomerization treatment is especially adapted for improving the drying properties of the polyhydric alcohol esters of the fatty acid mixtures obtained 20 from such vegetable oils as linseed oil, soya bean oil, chia seed oil, perilla oil, poppy seed oil, cottonseed oil, sunflower seed oil and the like as well as the poly-unsaturated fatty acids of fish oils, and 25 other polyunsaturated fatty acids having 18 or more carbon atoms in the molecule. As a practical matter the oils from which the fatty acids are obtained should have a relatively high iodine value, at least of 30 the order of 110—130, as otherwise there are not sufficient polyunsaturated acids present to warrant the treatment. It should also be noted that there is no 35 advantage in applying the isomerization process to eleostearic acid or to oils such as tung oil or oiticica oil which contain 40 large quantities of polyunsaturated acids having double bonds that are already in conjugation, although the treatment of 45 such acids is not excluded from the invention in its broadest aspects. Thus, for example, a mixture of 75 parts by weight of tung oil acids, was heated with 75 parts of potassium hydroxide and 100 50 parts of distilled water in an autoclave at 225—230° C. for 2.5 hours and liberated the resulting isomerized fatty acids from their potassium soaps. The resulting 55 amber coloured acids were partly liquid at room temperature, whereas the original acids were crystalline, and fractionation of the isomerized acids by distillation at 250—300° C. under 1 mm. pressure followed by analysis of the 60 fractions showed that the degree of triple 65

conjugation characteristic of eleostearic acid had been substantially reduced while corresponding quantities of acids having only double conjugation had been formed. While this constitutes further 70 proof that the conditions obtaining during the heating step brought about equilibrium favouring double conjugation, esterification of the isomerized tung oil acids with glycerine did not give 75 as good a drying oil as the original tung oil.

In many cases it is feasible to subject higher fatty acid mixtures having a relatively low content of polyunsaturated 80 fatty acids to a preliminary treatment that will separate out the more highly saturated fatty acids such as stearic acid, palmitic acid and the like. Thus, for example, the crude fatty acids obtainable 85 by saponification of soya bean oil, upon refrigeration at about 4° to 12° below zero, Centigrade, for 24 hours will crystallize out substantial quantities of stearic and palmitic acids, which can be 90 removed by filtration, and the percentage of doubly unsaturated fatty acids in the remaining oil is of course increased substantially.

The content of fatty acids having conjugated double bonds can also be increased by vacuum distillation of the isomerized fatty acid mixtures. It has been found that the acids in which conjugation has occurred have slightly higher boiling 100 points at reduced pressures than the corresponding non-conjugated acids, so that fractions rich in conjugated acids can be separated by this method. Ordinarily a flash distillation is preferred, 105 as considerable polymerization of the conjugated acids is encountered if they are maintained at elevated temperatures for too long a time.

Another feature of the invention which 110 is important from a commercial point of view resides in the direct treatment of glyceride oils themselves by the alkali isomerization process. When such triglycerides as soya bean oil, linseed oil, 115 perilla oil and the like are charged into an autoclave and heated with an aqueous solution of an alkali the oil is immediately saponified and the soaps of its fatty acids are formed. When the solution contains 120 an excess of alkali over that necessary to saponify all the fatty acids and sufficient water to dissolve the resulting soaps it is unnecessary to carry out the saponification as a separate step, but the autoclave 125 may be directly heated to 200—250° C. and the contents maintained at these temperatures until conjugation of the double bonds of the fatty acids is effected.

After the isomerization of the fatty 130

acids has been effected by the above described or similar processes, drying oils of improved characteristics are obtained by esterifying the isomerized acids with 5 a polyhydric alcohol. Any alcohol of this class having three or more esterifiable hydroxy groups may be used for this purpose, such as glycerol, pentaerythritol or dipentaerythritol. We are aware that 10 dehydrated castor oil fatty acids, containing from 20 to 30% of octadecadienic 9, 11 acid-1, have been esterified with glycerine and other polyhydric alcohols for the production of drying oils, and 15 that other unsaturated fatty acids have been isomerized to a certain extent by refluxing with alcoholic potash. On the other hand certain new oils of improved drying properties are obtained by the new 20 isomerization process, notably those resulting from the treatment of soya bean oil and linseed oil and their fatty acids. These isomerized acids contain about 34—40% or more of doubly conjugated 25 fatty acids, and those from linseed oil also contain about 8—15% of triply conjugated acids, and their esters with glycerine and other polyhydric alcohols possess correspondingly improved drying 30 properties.

It should be understood that conjugation of all the double bonds present in polyunsaturated higher fatty acids is not usually obtained by the process of the 35 invention. The point of equilibrium between the conjugated and non-conjugated acids seldom exceeds 50%, and therefore only about half of the dienic or polyenic acids of the oils are isomerized. 40 However, the polyhydric alcohol esters of fatty acid mixtures that have been isomerized to this extent exhibit faster and better drying properties as well as heat-bodying characteristics than are 45 possessed by the original oils from which these acids were obtained, and since the isomerization equilibrium can be attained rapidly in ordinary equipment this improvement is relatively inexpensive. 50

When the isomerization treatment is applied to the fatty acids of linseed oil and to dehydrated castor oil fatty acids, it has been found that the resulting fatty 55 acid mixtures have very similar properties. By preparing the esters of the isomerized fatty acids from these two sources with glycerine, pentaerythritol and dipentaerythritol there have been 60 obtained new drying oils which contain about 40% of esterified octadecadienic acids in which the two double bonds are in conjugation. These oils have excellent drying properties, and are included as 65 specific features of the present invention.

The invention will be illustrated in greater detail by reference to the following specific examples. The results obtained in these examples were evaluated by the spectroscopic method referred to 70 in Volume 37 of the Biochemical Journal, pages 138—141 (1937) and described in greater detail in Industrial & Engineering Chemistry, Volume 32 (1940), page 963. By this means it was possible to 75 make quantitative determinations of the content of doubly, triply and quadruply conjugated higher fatty acids in fatty acid mixtures within very narrow limits of error. It should be understood, however, that while these examples may describe in detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader 80 aspects is not limited thereto. 85

In Examples 2, 3, 4 and 7 some of the isomerized fatty acids have been described by name. It is quite possible, however, that the conjugated double bond systems 90 of these acids may be one or two carbon atoms removed from the positions assigned, and therefore these examples should be regarded as indicative of the results obtained rather than as proof of 95 the exact structural formulae of these compounds.

EXAMPLE 1.

75 parts by weight of linseed fatty acids, 75 parts by weight of 100% 100 potassium hydroxide and 100 parts by weight of water were charged into a stainless steel bomb-type autoclave fastened in an electrically heated chamber mounted on a rocking device to 105 provide continuous agitation. The degree of heating was thermostatically controlled and recorded by a recording pyrometer. The mixture was heated with agitation to 225° C. in 45 minutes, after which it rose 110 to 240° C. but dropped rapidly again to 225° C. where it was held for 1.75 hours. The autoclave was then opened and the soft soap and alkali dissolved in an excess of distilled water and decomposed by 115 agitation with excess hydrochloric acid at the boiling point. The liberated fatty acids were again treated with hydrochloric acid to ensure complete hydrolysis of the soaps, after which the product was 120 again washed with distilled water and dried.

The refractive index of the product was 1.4782 at 25° C. as compared with the value of 1.4690 of the linseed fatty acids 125 before the alkali treatment. When analyzed for doubly and triply conjugated double bonds by determining the ultraviolet absorption spectra in 0.2%—5% cyclohexane solutions the product 130

was found to contain 34.6% of 9, 11-octadecadienic acid-1 and 7.66% of 10, 12, 14-octadecatrienic acid-1 or conjugated isomers of these.

5 28 parts by weight of the isomerized fatty acid mixture was reesterified by heating with 10.2 parts of 95% glycerine in an atmosphere of carbon dioxide at 215—220° C. for 6 hours. The product 10 was a clear yellow oil which air dried overnight when mixed with driers and flowed out on tin panels. Similar films

hardened within a few hours when stoved at 100° C.

EXAMPLE 2.

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100 parts by weight of soya bean fatty acids, 75 parts of potassium hydroxide and 110 parts of water were charged into the autoclave described in Example 1 and heated with agitation at 225° C. for 2.5 20 hours. Analysis of the fatty acids before and after the isomerization gave the following results:—

25	$n/25^{\circ}\text{C.}$	D	
		9,11-Octadecadienic Acid-1	10,12,14-Octadecatrienic Acid-1
Before treatment	- - -	1.4641	1.05%
After treatment	- - -	1.4676	20.20% 0.165% 1.330%

30 Samples of the isomerized fatty acid mixture were esterified with glycerine and with pentaerythritol by heating them at 215—225° C. with a 5% excess of the alcohol over that necessary to form the neutral ester. The drying properties of the triglyceride oil were considerably 35 better than those of soya bean oil, which dries slowly to a soft film, while the pentaerythritol ester had even better drying properties than the triglyceride.

than the potassium soap of Example 1 and a little more difficult to hydrolyze, but otherwise the results were similar. 50 The dried isomerized fatty acids had a refractive index of 1.4803 and contained 41.0% of 9, 11-octadecadienic acid-1 and 8.2% of 10, 12, 14-octadecatrienic acid-1 or conjugated isomers thereof. 55

EXAMPLE 4.

40 75 parts by weight of linseed fatty acids, 75 parts of 100% sodium hydroxide and 125 parts of water were heated at 220—225° C. under 150—170 lbs. per sq. in. gauge pressure for three hours and 45 then cooled, dispersed in water, and treated with hydrochloric acid as before. The sodium soap was somewhat harder

100 parts by weight of fish-oil fatty acids (a product known commercially as Neo-Fat #19 acids) and 75 parts by weight of lithium hydroxide were charged 60 into the autoclave of Example 1 together with 100 parts of water. The batch was heated at 215—220° C. for 3.5 hours after which the product was acidified, washed, and the fatty acids recovered in the usual 65 manner. Analysis showed the materials before and after treatment to contain:—

70	$n/25^{\circ}\text{C.}$	D		
		9,11-Octadecadienic Acid-1	10,12,14-Octadecatrienic Acid-1	Conjugated acid with 4 double bonds
Before treatment	- - -	1.4797	3.13%	1.7% 0.14%
After treatment	- - -	1.4906	23.20% 8.0%	2.30%

75 The formation of a conjugated acid with four double bonds and a trace of a five double bonded acid distinguishes this from the preceding batches and is due to the fact that many fish oils (unlike most vegetable oils) contain substantial amounts of the more highly unsaturated 80 acids.

When esterified with a small excess of glycerine the isomerized fish oil acids formed a triglyceride having excellent drying properties. An alkyd resin prepared by heating together 30 parts of phthalic anhydride, 19 parts of glycerine and 56 parts of the isomerized acids at 220° C. for 3.5 hours, dried rapidly at 90° C. when dissolved in mineral spirits

90 and flowed on tin panels. The dried film had a frosted appearance similar to that obtained in tung oil formulations, which constituted further proof of conjugation of the double bonds.

EXAMPLE 5.

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It is known that castor oil fatty acids can be dehydrated by heating at about 280° C., and that the resulting product contains about 15—30% of conjugated double bonds in the form of octa- 100 decadienic-9, 11-acid-1. The following example shows that the content of conjugated double bonds can be greatly increased by applying the principles of the present invention. 105

75 parts by weight of dehydrated castor oil fatty acids, 75 parts by weight of lithium hydroxide and 100 parts of water were charged into the autoclave of 5 Example 1 and heated with agitation. The temperature was raised to 20° C. in 45 minutes and held at 220-225° C. for three hours. The soaps were then recovered, hydrolyzed with hydrochloric acid and water, washed free from mineral acid and dried over anhydrous calcium chloride. The refractive index of the acids before the treatment was $n/25^{\circ}\text{D}$ = 1.4706; after the 10 treatment it was 1.4734. The recovered light amber-coloured acids were distilled at 1-2 mm. of mercury yielding an almost water-white product of $n/25^{\circ}\text{D}$ = 1.4731 in 15 93% yield. Analysis of the alkali-treated, distilled acids by determining their absorption spectra showed them to contain 41.7% of conjugated double bonds as compared with 26.0% determined for the original acids by the same 20 method.

EXAMPLE 6.

In all the foregoing examples sufficient

alkali was used to form water-soluble soaps of the unsaturated fatty acids. The following example shows that isomerization is not obtained when this condition is not observed.

The autoclave of Example 1 was charged with 100 parts by weight of 35 linseed fatty acids, 120 parts of water and only 5 parts of sodium hydroxide, which was just enough to form sufficient soap to emulsify the excess fatty acids in the water. This batch was heated in the 40 autoclave at 220° C. for three hours and then hydrolyzed with acid, washed and recovered in the usual manner. The refractive index of the dried acids was 1.4690, which was identical with that of 45 the starting material, from which it was apparent that no conjugated unsaturation had been developed.

EXAMPLE 7.

The content of conjugated isomers in 50 the alkali isomerized fatty acids of the invention can be still further increased by vacuum distillation. Samples of the products of Examples 3 and 4 were distilled at 1 mm. of mercury absolute 55 pressure and the following cuts obtained:—

TABLE I.
PRODUCT OF EXAMPLE 3.

Material	% Yield	$n/25^{\circ}\text{D}$	n-octadecanoic acid		
			Description.	9,11-diene	10,12,14-trienic
Original	—	1.4803	Brown liquid & white solid	41.0	8.2
1st cut to 170° C.	8	1.4635	White solid	23.0	3.1
2nd cut 170—180° C.	71	1.4715	Water white liquid	40.4	6.8
3rd cut 180—190° C.	7	1.4830	Light yellow liquid	43.1	18.8
Residue	10	1.4995	Brown tar	—	—

TABLE II.
PRODUCT OF EXAMPLE 4.

Material	% Yield	$n/25^{\circ}\text{D}$	n-octadecanoic acid		
			Description	9,11-dienic	10,12,14-trienic
Original	—	1.4906	Amber liquid	23.2	8.0
1st cut to 175° C.	10	1.4540	Solid }	13.9	2.65
2nd cut 175—195° C.	36	1.4656	Solid }	25.6	6.0
3rd cut 195—210° C.	34	1.4691	Lemon liquid	20.4	6.2
4th cut 200—210° C.	4	1.4975	Yellow liquid	—	1.12
Residue	16	—	Brown tar	—	—

These tables show that a product containing 5 to 10% more doubly conjugated fatty acids can be obtained by separating the higher boiling fatty acids from those

of lower boiling point by simple distillation. The relatively large quantities of tar indicate that much better and more efficient results are obtainable when 90

pressures considerably lower than 1 millimeter of mercury are employed with a corresponding reduction in the distillation temperature and the amount of polymerization. Continuous distillation of the alkali isomerized fatty acids in a molecular still, for example, under a vacuum of 2 to 3 microns absolute mercury pressure will result in more complete separation of the various acids and in less loss by polymerization.

EXAMPLE 8.

The second and third cuts of Table I of Example 7, amounting to 78% of the total, were combined. 40 parts by weight of the mixture were heated with 4 parts of glycerine at 215° C. with continuous agitation while maintaining an atmosphere of carbon dioxide to avoid discolouration. After 5 hours the acid number of the batch was 25.3. Heating was then continued for an additional 1.75 hours whereupon a light-coloured oil was obtained having an acid number of 23.25. This was heated to 220—240° C. for 20 minutes in order to remove free acid, after which the acid number was 7.8 and the refractive index at 25° C. was 1.4875.

10 gram samples of the resulting

synthetic drying oil were mixed with 30 0.8 cc. of a drier containing 5% Pb and 0.5% Co. These samples were flowed out on tin panels, two of which were air dried while two more were baked at 100° C., both in comparison with similar 35 panels coated with linseed oil containing similar amount of drier. The synthetic oil containing the isomerized fatty acids was found to have a faster initial set than the natural oil on air drying, while on 40 the baked panels it seemed at first to be more tacky than the natural oil but finally, after continued baking, both oils cured to water-resistant films.

EXAMPLE 9.

45 Oil modified alkyd resins were made from representative drying oil acids before and after isomerization by heating together 56 parts by weight of the acid, 29.6 parts of phthalic anhydride and 18.8 50 parts of glycerol.

This mixture was heated in an atmosphere of carbon dioxide at 180—230° C. for 3.5 hours until the acid number of the product was about 29. 55 Four resins were prepared in this manner having the following characteristics:—

Resin No.	Fatty Acid Used	Acid No. of Solids	Viscosity (75% in Xylene)
60	1 Linseed	34	1.40 Poises
	2 Isomerized Linseed, Example 1	28	5.50 ,
	3 Soya bean	31	1.10 ,
65	4 Isomerized Soya, Example 2	26	1.80 ,

These resins were dissolved in approximately an equal weight of mineral spirits, flowed on tin panels, and stoved for half an hour without the addition of 70 a drier. Resin 2 was found to set up faster than resin 1, and resin 4 set faster than resin 3, with better through dry and less tack. It is evident, therefore, that isomerized fatty acids prepared by the 75 methods of the present invention are well suited for use in the preparation of drying resins.

EXAMPLE 10.

883 parts by weight of linseed fatty acids, isomerized by the method described in Example 3 and distilled and containing 31.4% higher fatty acids having doubly conjugated double bonds and 7.3% of acids having triply conjugated

double bonds, were esterified with 141 85 parts by weight of dipentaerythritol by heating at 200—205° C. for 6.75 hours. The crude esterification product had an acid number of 17.9 which, after two extractions with anhydrous ethanol, was 90 reduced to 3.1.

This ester was tested for gelation in comparison with a dipentaerythritol ester of ordinary unisomerized linseed acids, washed twice with anhydrous ethanol, 95 and also with a commercial triglyceride ester of dehydrated castor oil fatty acids. 10 g. samples of the three synthetic oils in test tubes were prepared in an oil bath, the temperature of which was raised 100 to 250° C. in one hour and thereafter maintained at 250° C. The results obtained are shown in the following table:—

Material	Time at 250° C.	Viscosity
Isomerized Linseed Dipentaerythritol ester	3 hours	Firm gel
Linseed Dipentaerythritol ester	5.5 hours	Z = 22.7 poises
Dehydrated castor oil Triglyceride	5.5 hours	U = 6.27 poises

From the foregoing results it is evident that the dipentaerythritol ester of the isomerized linseed oil fatty acids, due to its extreme polyfunctionality and conjugated unsaturation, sets up much faster than the corresponding ester of ordinary linseed oil fatty acids, and that a much more completely polymerized product is obtained.

EXAMPLE 11.

Linseed oil fatty acids were isomerized by stirring together 100 parts by weight of the acids, 100 parts of water, and 25 parts of 85% potassium hydroxide until a soap paste was formed and heating in an agitated autoclave at 225° C. for 3.75 hours. The soaps were then hydrolyzed with hydrochloric acid at the boiling point of the aqueous solution and the fatty acids were separated, washed and dehydrated. The acids were then found to contain 33.1% of doubly conjugated and 11.5% of triply conjugated acids, whereas the original material had contained 1.81% and 0.253% respectively.

62 parts of these acids were mixed with 10.1 parts of dipentaerythritol and heated with agitation in an atmosphere of carbon dioxide. The temperature was carried to 180° C. in one hour, then to 200° C. during the second hour and maintained at this point for 5 hours longer, when the acid number was found to be 11.3. The ester was then extracted twice with anhydrous ethanol, recovered and dried. It had an acid number of 2.1, viscosity of Y (Gardner) and colour of 4 (Hellige).

Upon addition of driers containing 0.5% Pb + 0.05% Mn + 0.005% Co as metal to oil and flowing out on a tin plate the ester was medium set in one hour, had a very slight tack for the next 4 hours, and was tack-free in 6 hours. After air drying for 24 hours it showed only a very slight whitening when immersed in distilled water.

In Specification No. 561,803, which though published after the date of the present application, was deposited pursuant to an application which is of prior date thereto, there is claimed the process for the isomerization of unsaturated higher fatty acids containing at least two isolated ethylenic double bonds, whereby they are converted, to a sub-

stantial extent, into the conjugated form, which comprises heating the said acids under pressure in an aqueous medium, at a temperature of at least 120° C., with an excess over the chemical equivalent of a water-soluble alkaline reagent. It will be appreciated that the present invention uses only temperatures of 200—250° C. and that the heating is discontinued before excessive polymerization of the unsaturated acids has taken place.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed (as communicated to me by my foreign correspondents), I declare that what I claim is:—

1. In a method of isomerizing higher aliphatic polyolefinic monocarboxylic acids to increase the degree of conjugated unsaturation thereof, the step of heating an aqueous solution of soaps thereof and an excess of alkali in a closed chamber at temperatures of 200—250° C. and under the corresponding autogenic pressure for a period of time sufficient to effect substantial conjugation in the polyunsaturated higher aliphatic monocarboxylic acids and discontinuing the heating before excessive polymerization of the unsaturated acids has taken place.

2. A method according to Claim 1 in which there is used a naturally occurring vegetable oil having an iodine number of at least 110, such as soya bean oil or linseed oil, or the fatty acids thereof, or fish oil fatty acids.

3. A method according to either of Claims 1 and 2 in which the resulting mixture of soaps is acidified and the liberated fatty acids are separated by vacuum distillation.

4. The improved method of isomerizing polyunsaturated higher aliphatic monocarboxylic acids substantially as hereinbefore described with reference to any one of Examples 1—5.

5. A method for the production of a drying oil which comprises isomerizing a higher aliphatic polyolefinic monocarboxylic acid according to the method of any one of the preceding claims and esterifying the product with a polyhydric alcohol containing at least three esterifiable hydroxyl groups.

6. Isomerized higher fatty acids when-

ever prepared in accordance with the method of any one of Claims 1 to 4.

7. A drying oil whenever produced by the method of Claim 5.

Dated this 15th day of October, 1941.
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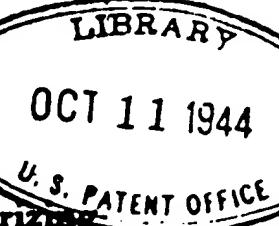
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Improvements in or relating to Methods of Isomerizing Polyunsaturated Fatty-Acids and to Drying Oils prepared therefrom

Communication from AMERICAN CYANAMID COMPANY, a Corporation organised under the laws of the State of Maine, United States of America, of 30, 5 Rockefeller Plaza, City and State of New York, United States of America.

I, ARTHUR HAROLD STEVENS, B.Sc. (Lond.), F.C.S., Fellow of the Chartered Institute of Patent Agents, a Subject of 10 the King of Great Britain, of the Firm of Stevens, Langner, Parry & Rollinson, of 5/9, Quality Court, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention, and in what 15 manner the same is to be performed, to be particularly described and ascertained in and by the following statement: —

This invention relates to improvements in drying oils and the higher fatty acids 20 which they contain. The invention includes the preparation of such oils by isomerizing polyunsaturated higher fatty acids to bring about a relatively high content of conjugated double bonds therein 25 followed by esterification of the isomerized acids with a polyhydric alcohol. The invention also includes a new and improved method of isomerizing polyunsaturated fatty acids as well as certain new 30 drying oils prepared therefrom.

It is known that the drying properties of polyunsaturated higher fatty acids, when employed in the form of triglycerides, oil-modified alkyl resins and the 35 like, are influenced by the positions of their double bonds with respect to each other. If these double bonds are in conjugation (i.e. separated by only one single bond) the oil has better drying properties 40 than a similar oil having an equal number of non-conjugated double bonds. Thus, for example, tung oil dries faster than linseed oil because the three double bonds of the eleostearic acid found in tung 45 oil are in conjugation whereas the double bonds of the linoleic and linolenic acids of linseed oil are not. It is a principal object of the present invention to provide a relatively quick and inexpensive method 50 of isomerizing polyunsaturated higher fatty acids to bring the double bonds

thereof into conjugation so that the polyhydric alcohol esters thereof will have improved drying properties.

The present invention provides in a 55 method of isomerizing higher aliphatic polyolefinic monocarboxylic acids to increase the degree of conjugated unsaturation thereof, the step of heating an aqueous solution of soaps thereof and an excess of alkali in a closed chamber at temperatures of about 200—250° C. and under the corresponding autogenous pressure for a period of time sufficient to effect substantial conjugation in the polyunsaturated higher aliphatic monocarboxylic acids and discontinuing the heating before excessive polymerization of the unsaturated acids has taken place.

It has been found that the double bonds 70 of polyunsaturated higher fatty acids are brought into conjugation within a few hours by heating an aqueous solution of the soaps thereof with excess alkali in a pressure vessel at temperatures above 75 about 200° C. and under the corresponding autogenous pressures. It has also been found that by heating the acids at these temperatures in the form of a solution of their soaps in water the isomerization or 80 rearrangement of the double bonds proceeds much faster than would otherwise be the case, and an equilibrium favouring a relatively high content of conjugated double bonds is reached in from one to three hours. The most favourable temperature range appears to be from 200° to 85 250° C. for above this range excessive losses of the acids by polymerization may occur.

Insofar as it has been possible to determine, the invention is perfectly general in character and may be used for the isomerization of any unsaturated fatty acid or acids the molecules of which contain at least two non-conjugated double bonds. In most cases the isomerization treatment will be applied to mixed fatty acids only some of which are polyunsaturated as this is in the form in which these 100 acids are found in vegetable and fish oils of relatively high iodine values. It is an

important advantage of the invention, however, that it can be applied with success to fatty acid mixtures containing relatively low percentages of non-conjugated, polyunsaturated fatty acids, as is the case in soya bean fatty acids, as well as to the more highly polyunsaturated fatty acid mixtures such as those of linseed oil.

10 The isomerization treatment is especially adapted for improving the drying properties of the polyhydric alcohol esters of the fatty acid mixtures obtained from such vegetable oils as linseed oil, soya bean oil, chia seed oil, perilla oil, poppy seed oil, cottonseed oil, sunflower seed oil and the like as well as the polyunsaturated fatty acids of fish oils, and other polyunsaturated fatty acids having 18 or 20 more carbon atoms in the molecule. As a practical matter the oils from which the fatty acids are obtained should have a relatively high iodine value, at least of the order of 110—130, as otherwise there are not sufficient polyunsaturated acids present to warrant the treatment. It should also be noted that there is no advantage in applying the isomerization process to eleostearic acid, or to oils such as tung oil or oiticica oil which contain large quantities of polyunsaturated acids having double bonds that are already in conjugation, although the treatment of such acids is not excluded from the invention in its broadest aspects. Thus, for example, a mixture of 75 parts by weight of tung oil acids was heated with 75 parts of potassium hydroxide and 100 parts of distilled water in an autoclave at 225—40 230° C. for 2.5 hours and liberated the resulting isomerized fatty acids from their potassium soaps. The resulting amber coloured acids were partly liquid at room temperature whereas the original acids were crystalline, and fractionation of the isomerized acids by distillation at 250—300° C. under 1 mm. pressure followed by analysis of the fractions showed that the degree of triple conjugation characteristic of eleostearic acid had been substantially reduced while corresponding quantities of acids having only double conjugation had been formed. While this constitutes further proof that the conditions obtaining during the heating step brought about equilibrium favouring double conjugation, esterification of the isomerized tung oil acids with glycerine did not give as good a drying oil as the original tung oil.

In many cases it is feasible to subject higher fatty acid mixtures having a relatively low content of polyunsaturated fatty acids to a preliminary treatment 65 that will separate out the more highly

saturated fatty acids such as stearic acid, palmitic acid and the like. Thus, for example, the crude fatty acids obtainable by saponification of soya bean oil, upon refrigeration at about 4° to 12° below zero, Centigrade, for 24 hours will crystallize out substantial quantities of stearic and palmitic acid, which can be removed by filtration, and the percentage of doubly unsaturated fatty acids in the remaining oil is of course increased substantially.

The content of fatty acids having conjugated double bonds can also be increased by vacuum distillation of the isomerized fatty acid mixtures. It has been found that the acids in which conjugation has occurred have slightly higher boiling points at reduced pressures than the corresponding non-conjugated acids, so that fractions rich in conjugated acids can be separated by this method. Ordinarily a flash distillation is preferred, as considerable polymerization of the conjugated acids is encountered if they are maintained at elevated temperatures for too long a time.

Another feature of the invention which is important from a commercial point of view resides in the direct treatment of glyceride oils themselves by the alkali isomerization process. When such triglycerides as soya bean oil, linseed oil, perilla oil and the like are charged into an autoclave and heated with an aqueous solution of an alkali the oil is immediately saponified and the soaps of its fatty acids are formed. When the solution contains an excess of alkali over that necessary to saponify all the fatty acids and sufficient water to dissolve the resulting soaps it is unnecessary to carry out the saponification as a separate step, but the autoclave may be directly heated to 200—250° C. and the contents maintained at these temperatures until conjugation of the double bonds of the fatty acids is effected.

After the isomerization of the fatty acids has been effected by the above described or similar processes, drying oils of improved characteristics are obtained by esterifying the isomerized acids with a polyhydric alcohol. Any alcohol of this class having three or more esterifiable hydroxyl groups may be used for this purpose, such as glycerol, pentaerythritol or dipentaerythritol. We are aware that dehydrated castor oil fatty acids, containing from 20 to 30% of octadecadienoic 9, 11 acid-1, have been esterified with glycerine and other polyhydric alcohols for the production of drying oils, and that other unsaturated fatty acids have been isomerized to a certain extent by refluxing with alcoholic potash. On the other hand cer-

tain new oils of improved drying properties are obtained by the new isomerization process, notably those resulting from the treatment of soya bean oil and linseed oil and their fatty acids. These isomerized acids contain about 30-40% or more of doubly conjugated fatty acids, and those from linseed oil also contain about 8-15% of triply conjugated acids, and their esters with glycerine and other polyhydric alcohols possess correspondingly improved drying properties.

It should be understood that conjugation of all the double bonds present in polyunsaturated higher fatty acids is not usually obtained by the process of the invention. The point of equilibrium between the conjugated and non-conjugated acids seldom exceeds 50%, and therefore only about half of the dienic or polyenic acids of the oils are isomerized. However, the polyhydric alcohol esters of fatty acid mixtures that have been isomerized to this extent exhibit faster and better drying properties as well as heat-bodying characteristics than are possessed by the original oils from which these acids were obtained, and since the isomerization equilibrium can be attained rapidly in ordinary equipment this improvement is relatively inexpensive.

When the isomerization treatment is applied to the fatty acids of linseed oil and to dehydrated castor oil fatty acids, it has been found that the resulting fatty acid mixtures have very similar properties. By preparing the esters of the isomerized fatty acids from these two sources with glycerine, pentaerythritol and dipentaerythritol there have been obtained new drying oils which contain about 40% of esterified octadecadienic acids in which the two double bonds are in conjugation. These oils have excellent drying properties, and are included as specific features of the present invention.

The invention will be illustrated in greater detail by reference to the following specific examples. The results obtained in these examples were evaluated by the spectroscopic method referred to in Volume 37 of the Biochemical Journal, pages 138-141 (1937) and described in greater detail in Industrial and Engineering Chemistry, Volume 32 (1940), page 963. By this means it was possible to make quantitative determinations of the content of doubly, triply and quadruply conjugated higher fatty acids in fatty acid mixtures within very narrow limits of error. It should be understood, however, that while these examples may describe in detail some of the more specific features of the invention, they are given primarily for purposes of illustration and

the invention in its broader aspects is not limited thereto.

In Examples 2, 3, 4 and 7 some of the isomerized fatty acids have been described by name. It is quite possible, however, that the conjugated double bond systems of these acids may be one or two carbon atoms removed from the positions assigned, and therefore these examples should be regarded as indicative of the results obtained rather than as proof of the exact structural formulae of these compounds.

EXAMPLE 1.

75 parts by weight of linseed fatty acids, 75 parts by weight of 100% potassium hydroxide and 100 parts by weight of water were charged into a stainless steel bomb-type autoclave fastened in an electrically heated chamber mounted on a rocking device to provide continuous agitation. The degree of heating was thermostatically controlled and recorded by a recording pyrometer. The mixture was heated with agitation to 225° C. in 45 minutes, after which it rose to 240° C. but dropped rapidly again to 225° C. where it was held for 1.75 hours. The autoclave was then opened and the soft soap and alkali dissolved in an excess of distilled water and decomposed by agitation with excess hydrochloric acid at the boiling point. The liberated fatty acids were again treated with hydrochloric acid to ensure complete hydrolysis of the soaps, after which the product was again washed with distilled water and dried.

The refractive index of the product was 1.4782 at 25° C. as compared with the value of 1.4690 of the linseed fatty acids before the alkali treatment. When analyzed for doubly and triply conjugated double bonds by determining the ultraviolet absorption spectra in 0.2%-5% cyclohexane solutions the product was found to contain 34.6% of 9,11-octadecadienic acid-1 and 7.66% of 10,12,14-octadecatrienic acid-1 or conjugated isomers of these.

28 parts by weight of the isomerized fatty acid mixture was re-esterified by heating with 10.2 parts of 95% glycerine in an atmosphere of carbon dioxide at 215-220° C. for 6 hours. The product was a clear yellow oil which air dried overnight when mixed with driers and flowed out on tin panels. Similar films hardened within a few hours when stored at 100° C.

EXAMPLE 2.

100 parts by weight of soya bean fatty acids, 75 parts of potassium hydroxide and 110 parts of water were charged into the autoclave described in Example 1 and

heated with agitation at 225° C. for 2.5 hours. Analysis of the fatty acids before and after the isomerization gave the following results:

5	n/25° C. D	9,11-Octadecadienic Acid-1.	10,12,14-Octad- catrienic Acid-1.				
		1.4641	1.4676	1.05%	20.20%	0.165%	1.330%
Before treatment							
After treatment							

10 Samples of the isomerized fatty acid mixture were esterified with glycerine and 10 with pentaerythritol by heating them at 215-225° C. with a 5% excess of the alcohol over that necessary to form the neutral ester. The drying properties of the triglyceride oil were considerably 15 better than those of soya bean oil, which dries slowly to a soft film, while the pentaerythritol ester had even better drying properties than the triglyceride.

EXAMPLE 3.

20 75 parts by weight of linseed fatty acids, 75 parts of 100% sodium hydroxide and 125 parts of water were heated at 220-225° C. under 150-170 lbs. per sq. in. gauge pressure for three hours and 25 then cooled, dispersed in water, and treated with hydrochloric acid as before. The sodium soap was somewhat harder

than the potassium soap of Example 1 and a little more difficult to hydrolyze, but otherwise the results were similar. The 30 dried isomerized fatty acids had a refractive index of 1.4803 and contained 41.0% of 9,11-octadecadienic acid-1 and 32% of 10,12,14-octadecatrienic acid-1 or conjugated isomers thereof.

EXAMPLE 4.

100 parts by weight of fish-oil fatty acids (a product known commercially as Neo-Fat #19 acids) and 75 parts by weight of lithium hydroxide were charged 40 into the autoclave of Example 1 together with 100 parts of water. The batch was heated at 215-220° C. for 3.5 hours after which the product was acidified, washed, and the fatty acids recovered in the usual 45 manner. Analysis showed the materials before and after treatment to contain:

60	n/25 D	9,11-Octadecadienic acid-1.	Conjugated acid with double-bonds.	
			10,12,14-Octadecatrienic acid-1.	
Before treatment	1.4797	3.13%	1.7%	0.14%
After treatment	1.4906	23.20%	8.0%	2.30%

55 The formation of a conjugated acid with four double bonds and a trace of a 55 five double-bonded acid distinguishes this from the preceding batches and is due to the fact that many fish oils (unlike most 60 vegetable oils) contain substantial amounts of the more highly unsaturated acids.

When esterified with a small excess of 65 glycerine the isomerized fish oil acids formed a triglyceride having excellent drying properties. An alkyl resin prepared by heating together 30 parts of phthalic anhydride, 19 parts of glycerine and 56 parts of the isomerized acids at 70 220° C. for 3.5 hours, dried rapidly at 90° C. when dissolved in mineral spirits and flowed on tin panels. The dried film had a frosted appearance similar to that obtained in tung oil formulations, which 75 constituted further proof of conjugation of the double bonds.

EXAMPLE 5.

It is known that castor oil fatty acids can be dehydrated by heating at about 230° C., and that the resulting product 80 contains about 15-30% of conjugated double bonds in the form of octadecadiene-9, 11-acid-1. The following example shows that the content of conjugated double bonds can be greatly increased by applying the principles of the present invention.

75 parts by weight of dehydrated castor oil fatty acids, 75 parts by weight of lithium hydroxide and 100 parts of water 90 were charged into the autoclave of Example 1 and heated with agitation. The temperature was raised to 200° C. in 45 minutes and held at 220-225° C. for three hours. The soaps were then 95 covered, hydrolyzed with hydrochloric acid and water, washed free from mineral acid and dried over anhydrous calcium

chloride. The refractive index of the aqueous before the treatment was $n/25.6$ D.

= 1.4706; after the treatment it was 1.4734. The recovered light amber-coloured acids were distilled at 1-2 mm. of mercury yielding an almost water-white product of $n/25 = 1.4731$ in 93% yield.

Analysis of the alkali-treated, distilled acids by determining their absorption spectra showed them to contain 41.7% of conjugated double bonds as compared with 26.0% determined for the original acids by the same method.

EXAMPLE 6.

In all the foregoing examples sufficient alkali was used to form water-soluble soaps of the unsaturated fatty acids. The following example shows that isomerization is not obtained when this condition is not observed.

The autoclave of Example 1 was charged with 100 parts by weight of linseed fatty acids, 120 parts of water and only 5 parts of sodium hydroxide, which was just enough to form sufficient soap to emulsify the excess fatty acids in the water. This batch was heated in the autoclave at 220° C. for three hours and then hydrolyzed with acid, washed and recovered in the usual manner. The refractive index of the dried acids was 1.4690, which was identical with that of the starting material, from which it was apparent that no conjugated unsaturation had been developed.

EXAMPLE 7.

The content of conjugated isomers in the alkali isomerized fatty acids of the invention can be still further increased by vacuum distillation. Samples of the products of Examples 3 and 4 were distilled at 1 mm. of mercury absolute pressure and the following cuts obtained:

TABLE I.
PRODUCT OF EXAMPLE 3.

Material	% Yield.	$n/25$ D	Description.	n -octadecanoic acid.		
				9,11-diene.	10,12,14-triene.	10,12,14-triene.
Original	—	1.4803	Brown liquid & white solid	41.0	8.2	
1st cut to 170° C.	8	1.4635	White solid	23.0	3.1	
2nd cut 170—180° C.	71	1.4715	Water white liquid	40.4	6.8	
3rd cut 180—190° C.	7	1.4830	Light yellow liquid	4.31	18.8	
Residue	10	1.4995	Brown tar	—	—	

TABLE II.
PRODUCT OF EXAMPLE 4.

Material	% Yield.	$n/25$ D	Description.	n -octadecanoic acid.		
				9,11-diene.	10,12,14-triene.	more than 3.
Original	—	1.4906	Amber liquid	23.2	8.0	2.3
1st cut to 175° C.	10	1.4540	Solid }	13.9	2.65	0.33
2nd cut 175—195° C.	36	1.4656	Solid }	25.6	6.0	0.84
3rd cut 195—210° C.	34	1.4691	Lemon liquid	20.4	6.2	1.12
4th cut 200—210° C.	4	1.4975	Yellow liquid	—	—	—
Residue	16	—	Brown tar	—	—	—

These tables show that a product containing 5 to 10% more doubly conjugated fatty acids can be obtained by separating

the higher boiling fatty acids from those of lower boiling point by simple distillation. The relatively large quantities of

tar indicate that much better and more efficient results are obtainable when pressures considerably lower than 1 millimeter of mercury are employed with a corresponding reduction in the distillation temperature and the amount of polymerization. Continuous distillation of the alkali isomerized fatty acids in a molecular still, for example, under a vacuum of 2 to 3 microns absolute mercury pressure will result in more complete separation of the various acids and in less loss by polymerization.

EXAMPLE 8.

15 The second and third cuts of Table I of Example 7, amounting to 78% of the total, were combined. 46 parts by weight of the mixture were heated with 4 parts of glycerine at 215° C., with continuous agitation while maintaining an atmosphere of carbon dioxide to avoid discolouration. After 5 hours the acid number of the batch was 25.3. Heating was then continued for an additional 1.75 hours whereupon a light-coloured oil was obtained having an acid number of 23.25. This was heated to 220—240° C. for 20 minutes in order to remove free acid, after which the acid number was 7.8 and 30 the refractive index at 25° C. was 1.4875.

60

Resin No	Fatty Acid Used.
1	Linseed
2	Isomerized Linseed, Example 1
65 3	Soya bean
4	Isomerized Soy, Example 2

These resins were dissolved in approximately an equal weight of mineral spirits, 70 flowed on tin panels, and stoved for half an hour without the addition of a drier. Resin 2 was found to set up faster than resin 1, and resin 4 set faster than resin 3, with better through dry and less tack. 75 It is evident, therefore, that isomerized fatty acids prepared by the methods of the present invention are well suited for use in the preparation of drying resins.

EXAMPLE 10.

80 883 parts by weight of linseed fatty acids, isomerized by the method described in Example 3 and distilled and containing 31.4% higher fatty acids having doubly conjugated double bonds and 85 7.3% of acids having triply conjugated

10 gram samples of the resulting synthetic drying oil were mixed with 0.8 cc. of a drier containing 5% Pb and 0.5% Co. These samples were flowed out on tin panels, two of which were air dried while two more were baked at 100° C., both in comparison with similar panels coated with linseed oil containing similar amount of drier. The synthetic oil containing the isomerized fatty acids was 40 found to have a faster initial set than the natural oil on air drying, while on the baked panels it seemed at first to be more tacky than the natural oil but finally, after continued baking, both oils cured to 45 water-resistant films.

EXAMPLE 9.

Oil modified alkyd resins were made from representative drying oil acids before and after isomerization by heating 50 together 56 parts by weight of the acid, 29.6 parts of phthalic anhydride and 18.8 parts of glycerol.

This mixture was heated in an atmosphere of carbon dioxide at 180—230° C. for 3.5 hours until the acid number of the product was about 29. Four resins were prepared in this manner having the following characteristics:

Acid No. of Solids. (75% in Xylene).	Viscosity
34	1.40 poises
28	5.50 ..
31	1.10 ..
26	1.80 ..

double bonds, were esterified with 141 parts by weight of dipentaerythritol by heating at 200—205° C. for 6.75 hours. The crude esterification product had an acid number of 17.9 which, after two extractions with anhydrous ethanol, was reduced to 3.1.

This ester was tested for gelation in comparison with a dipentaerythritol ester of ordinary unisomerized linseed acids, 90 washed twice with anhydrous ethanol, and also with a commercial triglyceride ester of dehydrated castor oil fatty acids.

10 g. samples of the three synthetic oils 100 in test tubes were prepared in an oil bath, the temperature of which was raised to 250° C. in one hour and thereafter maintained at 250° C. The results obtained are shown in the following table:

105

Material.	Time at 250° C.	Viscosity.
Isomerized linseed Dipentaerythritol ester	3 hours	Firm gel
Linseed Dipentaerythritol ester	5.5 hours	$Z = 22.7$ poises
Dehydrated castor oil Triglyceride	5.5 hours	$U = 6.27$ poises

From the foregoing results it is evident that the dipentaerythritol ester of the isomerized linseed oil fatty acids, due to its extreme polyfunctionality and conjugated unsaturation, sets up much faster than the corresponding ester of ordinary linseed oil fatty acids, and that a much more completely polymerized product is obtained.

EXAMPLE 11.

Linseed oil fatty acids were isomerized by stirring together 100 parts by weight of the acids, 100 parts of water, and 25 parts of 85% potassium hydroxide until a soap paste was formed and heating in an agitated autoclave at 225° C. for 3.75 hours. The soaps were then hydrolyzed with hydrochloric acid at the boiling point of the aqueous solution and the fatty acids were separated, washed and dehydrated. The acids were then found to contain 33.1% of doubly conjugated and 11.5% of triply conjugated acids, whereas the original material had contained 1.81% and 0.253% respectively.

62 parts of these acids were mixed with 10.1 parts of dipentaerythritol and heated with agitation in an atmosphere of carbon dioxide. The temperature was carried to 180° C. in one hour, then to 200° C. during the second hour and maintained at this point for 5 hours longer, when the acid number was found to be 11.3. The ester was then extracted twice with anhydrous ethanol, recovered and dried. It had an acid number of 2.1, viscosity of Y (Gardner) and colour of 4 (Hellige).

Upon addition of driers containing 0.5% Pb + 0.05% Mn + 0.005% Co as metal to oil and flowing out on a tin plate the ester was medium set in one hour, had a very slight tack for the next 4 hours, and was tack-free in 6 hours. After air drying for 24 hours it showed only a very slight whitening when immersed in distilled water.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, (as communicated to me by my foreign correspondents), I declare that

what I claim is:—

1. In a method of isomerizing higher aliphatic polyolefinic monocarboxylic acids to increase the degree of conjugated unsaturation thereof, the step of heating an aqueous solution of soaps thereof and an excess of alkali in a closed chamber at temperatures of about 200—250° C. and under the corresponding autogenic pressure for a period of time sufficient to effect substantial conjugation in the polyunsaturated higher aliphatic monocarboxylic acids and discontinuing the heating before excessive polymerization of the unsaturated acids has taken place.

2. A method according to Claim 1 in which there is used a naturally occurring stable oil having an iodine number of at least 110, such as soya bean oil or linseed oil, or the fatty acids thereof, or fish oil fatty acids.

3. A method according to either of Claims 1 and 2 in which the resulting mixture of soaps is acidified and the liberated fatty acids are separated by vacuum distillation.

4. The improved method of isomerizing polyunsaturated higher aliphatic monocarboxylic acids substantially as hereinbefore described with reference to any one of Examples 1—5.

5. A method for the production of a drying oil which comprises isomerizing a higher aliphatic polyolefinic monocarboxylic acid according to the method of any one of the preceding Claims and esterifying the product with a polyhydric alcohol containing at least three esterifiable hydroxyl groups.

6. Isomerized higher fatty acids whenever prepared in accordance with the method of any one of Claims 1 to 4.

7. A drying oil whenever produced by the method of Claim 5.

Dated this 15th day of October, 1941.
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